

Application No.: 10/501,140

Amendment Dated: January 8, 2007

### **INTERVIEW SUMMARY**

Applicants wish to thank Examiner Berch for the helpful and courteous discussion with Applicants' Representative on March 22, 2007. During this discussion, the claims as amended were discussed. The Examiner indicated that the amendments appear to overcome the rejection as being indefinite.

**REMARKS**

Applicants respectfully request reconsideration of the application, as amended, in view of the following remarks.

The rejections of Claim 11 are moot in view of the cancellation of this claim.

The rejection of Claims 6-11 under 35 U.S.C. § 112, 2<sup>nd</sup> paragraph, is obviated by the amendment of the claims. The phrase "polymer-analogous reaction" is well known in the art as shown by the attached pages from Macromolecules by Hans-Georg Elias.

As requested by the Examiner, a new Declaration is attached herewith.


This application presents allowable subject matter, and the Examiner is kindly requested to pass it to issue. Should the Examiner have any questions regarding the claims or otherwise wish to discuss this case, he is kindly invited to contact Applicants' below-signed representative, who would be happy to provide any assistance deemed necessary in speeding this application to allowance.

Respectfully submitted,

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*Hans-Georg Elias*

# **Macromolecules**

**Volume 1: Chemical Structures and Syntheses**



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E4413  
2005

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v. 1

- Volume 1 Chemical Structures and Syntheses  
Volume 2 Industrial Polymers and Syntheses  
Volume 3 Physical Structures and Properties  
Volume 4 Processing and Applications of  
Polymers

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Polymer-analog reactions are called **functionalization** if they provide the polymer molecules with "functional groups". The term "functionalization" is sometimes used exclusively for the modification of chain ends, i.e., for chain analog reactions, especially those of living polymers (Section 8.3.7).

Polymer analog reactions are subdivided according to the nature of the groups, A, C, and N, molecules B and D, and the type of the desired endproduct:

- **Polymer analog reactions** are classic polymer transformations where poly(C) is the desired endproduct of the reaction of poly(A) with B.
- **Reactive resins** are crosslinked polymers with reactive groups that are used to synthesize D. Poly(C) is here an intermediate product that is recycled to Poly(A).
- **Polymer reagents** are electrically uncharged reactive resins.
- **Ion exchangers (ion exchange resins)** are charged polymer reagents that can exchange ions with low-molecular weight compounds.
- **Polymer complexes** result from the addition of B to poly(A) without release of D and without formation of covalent bonds between A and B; B may also be a polymer group. In most cases, B-A bonds are hydrogen bonds, dipole-dipole interactions, or hydrophobic bonds. However, complexes may also be formed via coordinative bonds or electron-deficient bonds, i.e., chemical bonds.
- **Stereocomplexes** are polymer complexes between differently configured poly(A) and poly(A') molecules where A and A' are monomeric units with the same constitution but different configuration. An example is the stereocomplex of isotactic and syndiotactic poly(methyl methacrylate). Such complexes neither need to be formed in the ratio 1:1 of constitutional groups nor do they necessarily crystallize. In the general case, they are not "racemic crystallizations".

#### 15.4.2 Acid-Base Reactions

Acid-base reactions between polymer molecules and low-molecular weight compounds differ in several aspects from those between two low-molecular weight compounds. For the latter, a simple relationship exists between the pH, the degree of dissociation,  $\alpha$ , and the degree of neutralization,  $\beta$ . The logarithm of the equilibrium constant,  $K = [\text{H}^+][\text{A}^-]/[\text{HA}]$ , of an acid HA is

$$(15-9) \quad \lg K = \lg [\text{H}^+] + \lg \{[\text{A}^-]/[\text{HA}]\}$$

Introduction of the definitions  $\text{pH} = -\lg [\text{H}^+]$  and  $\text{pK}_a = -\lg K$  transforms Eq.(15-9) into the **Henderson-Hasselbalch equation**:

$$(15-10) \quad \text{pH} = \text{pK}_a + \lg \{[\text{A}^-]/[\text{HA}]\} = \text{pK}_a + \lg \{(1 - \beta)/\beta\} = \text{pK}_a + \lg \{\alpha/(1 - \alpha)\}$$

where  $\beta = [\text{HA}]/([\text{HA}] + [\text{A}^-])$  = degree of neutralization of acid groups and  $\alpha = 1 - \beta$  the degree of dissociation.  $\beta$  is usually calculated from the amount of added base.

The Henderson-Hasselbalch equation must be modified for polymers because of additional electrostatic and statistical effects. An example is the different behavior of poly(acrylic acid),  $[-\text{CH}_2-\text{CH}(\text{COOH})-]_n$ , and its low-molecular weight counterpart, propi-

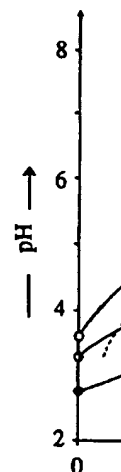


Fig. 15-3 pH as a function of the degree of neutralization for poly(acrylic acid), PAA, and propionic acid. With kinetic

onic acid,  $\text{H}-\text{CH}_2-\text{COOH}$ , the titration curves of poly(acrylic acid) and propionic acid (ppa) are shown. The neutral salts such as

This increase of the degree of neutralization of solutions, many of intramolecular repulsions between neighboring  $-\text{COO}^-$  groups become less stiff (i.e., the chains are more flexible) and  $\text{H}^+$  causes the  $-\text{COO}^-$  groups. By doing electrical work,  $\Delta G_{\text{el},0} = -2.303 RT$

$$(15-11) \quad \text{pH} = \text{pK}_a + \lg \{[\text{A}^-]/[\text{HA}]\}$$

In addition, there are other factors that compete with the electrostatic repulsion between the  $-\text{COO}^-$  groups. Such an effect is the degree of neutralization of protons; a fact, polyvalent acid

The presence of other ions in the solution shifts the titration curve parallel to the one of neutralization, po

provide the polymer sometimes used ex-reactions, especially

of the groups, A, C,

where poly(C) is the

that are used to syn-d to Poly(A).

agents that can ex-

without release of D ay also be a polymer ipole interactions, or ed via coordinative

configured poly(A) ith the same consti- plex of isotactic and r need to be formed ly crystallize. In the

ecular weight com- lecular weight com- he degree of dissoci- uilibrium constant,  $K$

ransforms Eq.(15-9)

$$a + \lg \{ \alpha / (1 - \alpha) \}$$

groups and  $\alpha = 1 - \beta$  of added base.

mers because of ad- ent behavior of poly- t counterpart, propi-

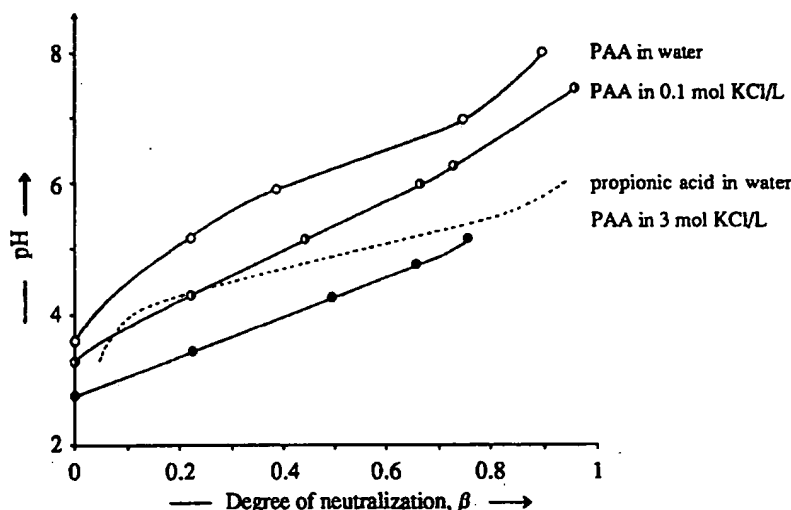


Fig. 15-3 pH as a function of the degree of neutralization,  $\beta$ , for the titration of 0.01 mol mer/L poly(acrylic acid), PAA, in water with or without addition of KCl. - - - pH =  $f(\beta)$  for 0.01 mol/L propionic acid. With kind permission by the American Chemical Society, Washington (DC) [2].

onic acid,  $\text{H}-\text{CH}_2-\text{CH}(\text{COOH})-\text{H}$ , on neutralization (Fig. 15-3). The pH of aqueous solutions of poly(acrylic acid) (PAA) is higher at all degrees of neutralization than that of propionic acid (ppA): poly(acrylic acid) is the weaker acid. At high concentrations of neutral salts such as KCl, it is just the opposite.

This increase of acid strength is caused by an electrostatic effect. In dilute aqueous solutions, many of the  $-\text{COOH}$  groups of PAA are dissociated to  $-\text{COO}^-$  and  $\text{H}^+$ . The intramolecular repulsion between  $-\text{COO}^-$  groups leads to a stiffening of PAA chains. Addition of a neutral salt pushes the protons more to the  $-\text{COO}^-$  groups. The repulsion between neighboring  $-\text{COO}^-$  groups is reduced and the poly(acrylic acid) molecules become less stiff (smaller radii of gyration). However, the closer proximity of  $-\text{COO}^-$  and  $\text{H}^+$  causes the latter to have a smaller effect on the dissociation of neighboring  $-\text{COO}^-$  groups. Because of the resistance of the strong electrostatic forces, additional electrical work,  $\Delta G_{el,0}$ , is now required to bring a proton from the chain backbone to an infinite distance from it. An additional Gibbs energy is required which can be written as  $\Delta G_{el,0} = -2.303 RT \lg K'$ . With  $\lg K' = -pK'_a$ , one obtains

$$(15-11) \quad \text{pH} = pK_a + \lg \{ (1 - \beta) / \beta \} + pK'_a = pK_a + \lg \{ (1 - \beta) / \beta \} + 0.434 \Delta G_{el,0} / (RT)$$

In addition, there is also a statistical effect because the protons of the acid groups compete with the cations of the added base for the available positions near  $-\text{COO}^-$  groups. Such an effect is known for low molecular weight dicarboxylic acids. Below a degree of neutralization of  $\beta = 0.5$ , more possibilities exist for dissociation than for association of protons; at  $\beta > 0.5$ , it is just the opposite. In the absence of the electrostatic effect, polyvalent acids should be stronger acids than the corresponding monovalent acids.

The presence of the statistical effect can be seen if the curves - - - and  $\bigcirc-\bigcirc$  are shifted parallel to the  $\beta$ -axis. However, the electrostatic effect dominates. At all degrees of neutralization, poly(acrylic acid) is therefore a weaker acid than propionic acid.

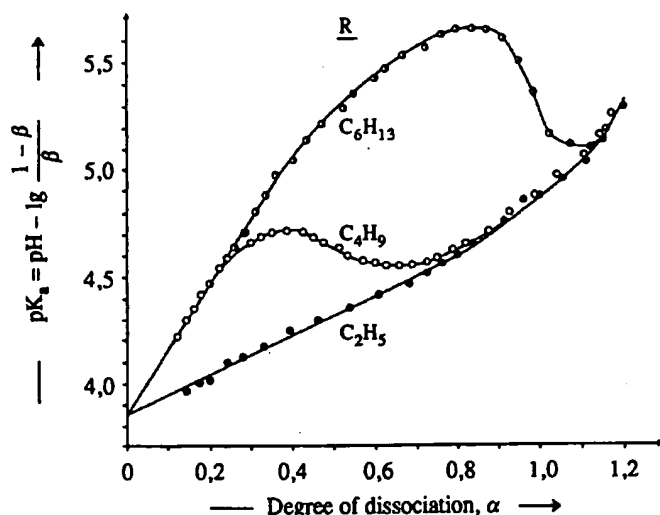


Fig. 15-4 Apparent values of  $pK_a$  of  $-\{CH(COOH)-CH(COOH)-alt-CH_2-CH(OR)-\}_n$  in water at  $30^\circ\text{C}$ . Data points for  $\text{C}_2\text{H}_5$  are symbolized by black dots, for  $\text{C}_4\text{H}_9$  by open circles, and for  $\text{C}_6\text{H}_{13}$  by half-filled circles. With kind permission by Kluwer Publications, New York [3].

Acid strengths of polyacids increase with decreasing size of nonhydrated counterions. As a consequence, polyacids bind more strongly to smaller lithium cations (higher charge density) than to larger rubidium ions (smaller charge density). The titration of a polyacid with  $\text{LiOH}$  solutions thus leads to a greater apparent acid strength.

Experiments have shown that the titration of polyacids with bases containing large cations requires ca. 20 % more base than one calculates for stoichiometric amounts. In osmotic, diffusion, and electrophoretic measurements, one also observes that polyions behave as if they bind great proportions of counter ions (sometimes up to 70 %!), i.e., as if a great proportion of counterions does not dissociate at all.

Additional effects are caused by hydrophobic bonds. For example, the polyacid from the saponified alternating copolymer of maleic anhydride and ethyl vinyl ether behaves completely normally in titrations (Fig. 15-4). However, maxima in the plots of apparent  $pK_a$  values as a function of the degree of dissociation,  $\alpha$ , were observed in the corresponding copolymers with butyl or cyclohexyl groups.

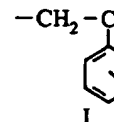
### 15.4.3 Ion Exchange

Ion-exchangers are inorganic or organic materials, usually in particle form, that are capable of reversibly exchanging their ions. Important inorganic ion exchangers include zeolites, montmorillonite, bentonites, etc. (Volume II). The bulk of industrially produced organic ion-exchange resins consists of crosslinked copolymers (PSX) from styrene S and divinyl benzenes DVB that have been functionalized.

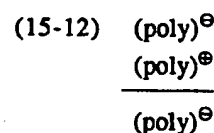
Treatment of the PSX with  $\text{SO}_3$  delivers very acidic cation exchange resins of the type  $(\text{poly})^\oplus$  (I). Reaction of PSX with chlorodimethyl ether and subsequent quaternation leads to II and that of PSX with *N*-chloromethyl phthalimide followed by saponification to III. Both II and III are strongly basic anion exchange resins of the type  $(\text{poly})^\ominus$ .

### 15 Reactions of Ma

Weakly acidic zenes and acrylic change resins are I



All ion exchange accessible. The disium reactions. Sa change resin, (poly



Regeneration of ion exchange resin

The ion exchange of dissociable groups accessible are the i ties are furnished their relatively open

The acid strength of hydrated counterions. The apparent effect is the opposite of hydrated ions is im

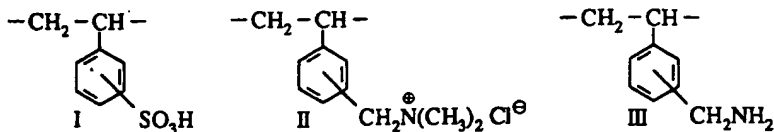
The effect is pronounced in crosslinked and uncrosslinked polymers, water is less available. This is possibly the case for poly(styrene sulfonate). This is possibly the case for a maximum with in

### 15.4.4 Polymer

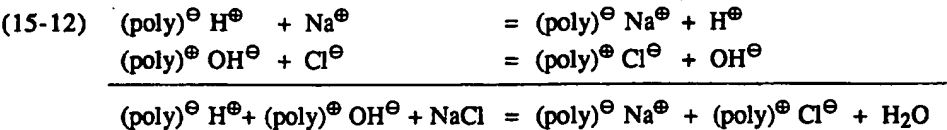
Polymer transformations of polymer are transformations in lowmolecular weight compounds: (1) conversion of modification of syn



Weakly acidic cation exchange resins are obtained from copolymers of divinyl benzenes and acrylic esters, followed by saponification with alkali. Many other ion exchange resins are known, for example, based on cellulose, phenolic resins, etc.



All ion exchange resins swell strongly in water whereupon dissociable groups become accessible. The dissociating low-molecular weight counterions are exchanged in equilibrium reactions. Salty water thus becomes desalted after passing through a cation exchange resin, (poly)<sup>⊖</sup> H<sup>⊕</sup>, and an anion exchange resin, (poly)<sup>⊕</sup> OH<sup>⊖</sup>:



Regeneration of (poly)<sup>⊖</sup> Na<sup>⊕</sup> by acids and (poly)<sup>⊕</sup> Cl<sup>⊖</sup> by bases restores the original ion exchange resins.

The ion exchange capacity is determined by the crosslinking density and the number of dissociable groups per monomeric unit. The higher the crosslinking density, the less accessible are the ionic groups and the higher the pK<sub>a</sub>. Especially high exchange capacities are furnished by macroreticular ion exchange resins (Section 16.5.1) because of their relatively open but rigid and less swellable structures.

The acid strength of crosslinked polyacids decreases with increasing size of the *hydrated* counterions. For example, hydrated lithium ions are larger than hydrated rubidium ions. The apparent acid strength of crosslinked polyacids is therefore greater in the presence of hydrated rubidium ions than in the presence of hydrated lithium ions. This effect is the opposite of that of *uncrosslinked* polyacids where the size of the *non-hydrated* ions is important (nonhydrated Rb<sup>⊕</sup> are larger than nonhydrated Li<sup>⊕</sup>).

The effect is probably caused by the different physical structures of water in cross-linked and uncrosslinked polymers. According to proton magnetic resonance measurements, water is less ordered in gels of poly(styrene sulfonic acid) than in uncrosslinked poly(styrene sulfonic acid). The degree of order varies with the degree of crosslinking. This is possibly the reason why the selectivity of charged gels toward ions passes through a maximum with increasing crosslink density.

15.4.4 Polymer Transformations

Polymer transformations are polymer modifications in which groups of the parent polymer are transformed into other groups in a manner similar to the corresponding reactions in lowmolecular weight compounds. They are performed in industry for two reasons: (1) conversion of inexpensive natural polymers into more useful ones and (2) modification of synthetic polymers because the desired chemical structures cannot be

Table 15-1 Industrial polymer transformations (without cyclizations, see Section 15.4.5). cell = Cellulose, E = ethylene unit, PVC = poly(vinyl chloride), VAc = vinyl acetate unit; \* = Chlorine content in %, \*\* % SO<sub>2</sub>Cl groups per ethylene group.

No.	Monomeric unit of parent polymer	Reagent	Conversion in %	Transformed monomeric unit	Application
1	CH <sub>2</sub> -CH(OOCCH <sub>3</sub> )	ROH	98	CH <sub>2</sub> -CHOH	thickener
2	ditto, E/VAc units	CH <sub>3</sub> OH	99	CH <sub>2</sub> -CHOH/CH <sub>2</sub> -CH <sub>2</sub>	engineering polymer
3	cell-NHCOCH <sub>3</sub>	H <sub>2</sub> O		cell-NH <sub>2</sub>	paper additive
4	cell-OH	CH <sub>3</sub> COOH	83-100	cell-OOCCH <sub>3</sub>	fibers, films
5	cell-OH	HNO <sub>3</sub>	67-97	cell-ONO <sub>2</sub>	plastics, etc. (see text)
6	cell-ONa	Oxirane	53-87	cell-OCH <sub>2</sub> CHRCH <sub>3</sub>	thickener
7	cell-OH	Oxirane	100-400	cell-OCH <sub>2</sub> CH(OR')CH <sub>3</sub>	thickener
8	CH <sub>2</sub> -CH <sub>2</sub>	Cl <sub>2</sub>	25-40* > 40*	CH <sub>2</sub> -CHCl CH <sub>2</sub> -CHCl + CHCl-CHCl	elastomers impact improver for PVC
9	CH <sub>2</sub> -CHCl	Cl <sub>2</sub>	64*	ditto	adhesive, lacquer
10	CH <sub>2</sub> -CH <sub>2</sub>	Cl <sub>2</sub> /SO <sub>2</sub>	< 42* < 2**	CH <sub>2</sub> -CHCl + CH <sub>2</sub> -CHSO <sub>2</sub> Cl (CH <sub>2</sub> ) <sub>4</sub> + CH <sub>2</sub> -CHCN	coatings elastomers
11	CH <sub>2</sub> CH=CHCH <sub>2</sub> + CH <sub>2</sub> -CHCN	H <sub>2</sub>			elastomers
12	N=PCl <sub>2</sub>	RONa		N=P(OR) <sub>2</sub>	elastomers

obtained by direct polymerization or only with high cost of monomers and processes. Table 15-1 lists 12 important examples:

1. Poly(vinyl alcohol) is not produced by polymerization of vinyl alcohol (or acetaldehyde, Section 7.4.2) but by transesterification of poly(vinyl acetate) with methanol or butanol. Methyl acetate and butyl acetate are sought after industrial solvents.

2. The partial ester exchange of acetate groups of poly(vinyl acetate-co-ethene)s delivers packaging films that are very impermeable to oxygen.

3. Saponification of the mucopolysaccharide chitin from the shells of *Crustaceae* produces chitosan (see Volume II) which is used as a paper additive.

4. Cellulose is esterified to cellulose (2 1/2)-acetate and cellulose triacetate by acetic acid. Both serve as fibers, the former also for cigarette filters.

5. Treatment of cellulose by nitrating acid (various mixtures of nitric acid and sulfuric acid) delivers cellulose nitrates with different degrees of nitration (formerly called "nitrocelluloses") that are used for nitro lacquers, guncotton, celluloid (in combination with camphor), etc.

6-7. Etherification of cellulose by ethylene oxide and/or propylene oxide leads to cellulose ethers. The etherification generates new OH groups. The degree of substitution may thus exceed 100 %.

8-10. Poly(ethylene), ethene-propene rubbers, and poly(vinyl chloride) are chlorinated and sulfochlorinated.

11. Butadiene-acrylonitrile rubbers (= nitrile rubbers) are hydrogenated which improves their resistance against aging.

12. Poly(dichlorophosphazene) (= phosphonitrile chloride) hydrolyzes easily. Reaction of the polymer with fluorinated alcohols delivers excellent specialty elastomers.

Polymer transformation of molecular weight of molecular structure of molecular weight of worse polymer product that proceed with This is one of the formations beside chlorination/sulfonation (see Table 15-1).

The second part activities of polymer their hydrogenation hydrolysis of polymer acetone/water (75, correct model con

~Cl

$k / (\text{L mol}^{-1} \text{min}^{-1})$

Rate constants at low-molecular intermolecular reaction very small proportion effects). The magnitude of the following exar

A 1 % solution of poly(vinyl alcohol) with a concentration of random coils in solution  $V_{\text{coil}} = 4 \pi r_3^3 M_u$  del such a coil is  $r = 20$  tion of groups in the the overall molar con

In homopolymers groups in -A-A-, in -A-A"-C-, or monomolecular rea

(15-13)  $-d[A]$

Depending on triads AAA, (AAC groups may have groups, or A-group and poly(A-block-relatively rare. But

ction 15.4.5). cell = Cel-  
nit; \* = Chlorine content

Application
thickener engineering polymer
paper additive fibers, films plastics, etc. (see text)
thickener thickener elastomers impact improver for PVC adhesive, lacquer coatings
elastomers
elastomers

omers and processes.

yl alcohol (or acetal-  
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solvents.

etate-co-ethene)s de-

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se triacetate by acetic

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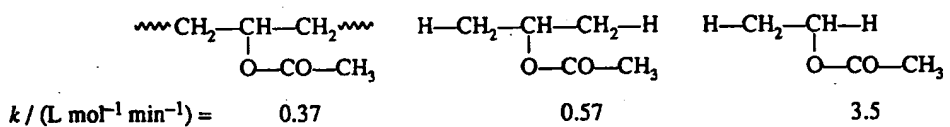
hloride) are chlorina-

lrogenated which im-

lolyzes easily. Reac-  
cialty elastomers.

Polymer transformations deviate from the corresponding transformations of low-molecular weight compounds in two respects. "By-products" become part of the macromolecular structure; they cannot be separated from the "main product" as in low-molecular weight chemistry. The resulting "wrong" chain units almost always lead to worse polymer properties. Industry therefore uses only those polymer transformations that proceed without side reactions or only with those that do not deliver unwanted ones. This is one of the main reasons why industry uses only four types of polymer transformations besides cyclization (Section 15.4.5): transesterification/ saponification (1-5), chlorination/sulfochlorination (8-10), etherification (6, 7, 12), and hydrogenation (11) (see Table 15-1). Oxidation, for example, always leads to degradation (Volume IV).

The second peculiarity is the often strong nearest neighbor effect. For this reason, reactivities of polymeric units should not be compared with those of their monomers or their hydrogenated monomers but with more appropriate compounds. An example is the hydrolysis of poly(vinyl acetate) and some model compounds by sodium hydroxide in acetone/water (75/25) at 30°C. The rate constants  $k$  indicate that isopropyl acetate is the correct model compound for vinyl acetate units but not ethyl acetate (or vinyl acetate).



Rate constants of polymer groups are furthermore only similar to those of appropriate low-molecular weight compounds if the polymer solution is very dilute (absence of intermolecular nearest neighbor effects) and the reactive polymeric units form only a very small proportion of the total ones (absence of intramolecular nearest neighbor effects). The magnitude of the first factor is often underestimated as can be seen from the following example.

A 1 % solution of ethyl acetate ( $M = 88 \text{ g/mol}$ ; degree of polymerization  $X_M = 1$ ) and a 1 % solution of poly(vinyl acetate) of  $M = 10^6 \text{ g/mol}$  ( $X_P = M/M_u = 10^6/86.5 \approx 11\,560$ ) are both solutions with a concentration of  $[\text{Ac}]_{\text{soln}} = 0.115 \text{ acetate groups per liter}$ . Poly(vinyl acetate) molecules form random coils in solution (Volume III). Approximation of coils as homogeneous spheres of volume  $V_{\text{coil}} = 4 \pi r^3 M_u / 3$  delivers a group concentration of  $C_{\text{coil}} = X/V_P = (3 M)/(4 \pi r^3 M_u)$ . The radius of such a coil is  $r = 20 \text{ nm}$ . The coil thus contains  $C_{\text{coil}} = 3.45 \cdot 10^{20} \text{ groups/mL}$ . The molar concentration of groups in the coil is therefore  $[\text{Ac}]_{\text{coil}} = C_{\text{coil}}/N_A \approx 0.57 \text{ mol/L}$  and thus 5 times as high as the overall molar concentration  $[\text{A}]_{\text{soln}} = 0.115 \text{ mol/L}$  of groups in solution.

In homopolymers with A-groups, reacting A-groups may be between two other A-groups in  $-\text{A}-\text{A}'-\text{A}-$ , between an A-group and a C-group (= already reacted A-group) in  $-\text{A}-\text{A}''-\text{C}-$ , or between two C-groups in  $-\text{C}-\text{A}'''-\text{C}-$ . The reaction rate of a pseudo-monomolecular reaction is thus

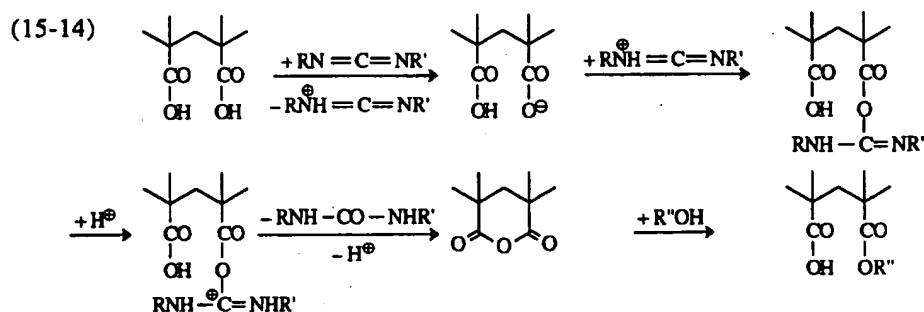
(15-13)  $-d[\text{A}]/dt = k'[\text{A}'] + k''[\text{A}''] + k'''[\text{A}'''] = k_{\text{app}}[\text{A}]$

Depending on the relative reactivity of the central A-group in the three different triads AAA, (AAC + CAA), and CAC, polymers with less than 100 % conversion of A-groups may have A-groups alternating with C-groups, randomly distributed A- and C-groups, or A-groups in long blocks. Of course, the two limiting cases, poly(A-alt-C) and poly(A-block-C) as well as the limiting case of a mixture of poly(A) and poly(C) are relatively rare. But they are not impossible as the following two examples show.

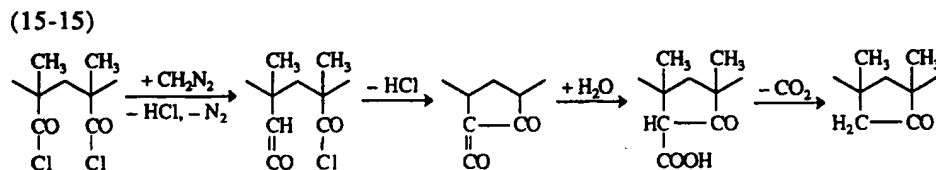
The saponification of poly(alkyl methacrylate)s delivers first polymers with randomly distributed  $-\text{COO}^-$  groups. These groups then induce the saponification of their nearest neighbors which leads to pseudocopolymers with blocks of methacrylic acid and alkyl methacrylate units.

The hydrogenation of poly(styrene) with Raney nickel as a catalyst leads initially to a conversion of only those phenyl groups that are in the vicinity of catalyst particles, i.e. to blocks of vinyl cyclohexane units and poly(styrene) units. If the vinyl cyclohexane blocks exceed a certain length, they will become incompatible with the styrene blocks (Volume IV) and phase separation results. If the chains with vinyl cyclohexane blocks are still near the catalyst, all styrene units in that chain will be hydrogenated. The result is a mixture of poly(styrene) chains and poly(vinyl cyclohexane) chains, i.e., a polymer blend of these two polymers and not partially hydrogenated poly(styrene) molecules.

More or less alternating pseudocopolymers are obtained only in those rare cases where suitable intermediates are formed. For example, the esterification of syndiotactic poly(methacrylic acid) by alcohols  $\text{R}'\text{OH}$  with the help of carbodiimides does not lead directly to the ester. Rather, an anhydride is formed first which then reacts with the alcohol to form a pseudocopolymer with alternating acid and ester groups:



Participating neighboring groups often lead to unexpected reaction products. For example, poly(methacrylochloride) does not react with diazomethane to form diazoketones as it is common for Arndt-Eistert reactions. Instead, intermediate  $\beta$ -ketoketene rings are obtained. Subsequent hydrolysis leads to the corresponding acid and finally, by decarboxylation, to cyclic ketones:



Reaction rates and maximum conversions are strongly influenced by the reaction media. At incomplete group transformation, all polymer analog reactions result in pseudocopolymers. These intermediates will precipitate if they are insoluble in the medium. The remaining unreacted groups are buried and cannot react. The resulting product is a pseudopolymer with a non-random distribution of substituents. In order to obtain complete (or nearly so) polymer analog reactions, solvents must be used that dissolve at least the completely converted reaction product.

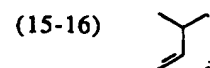
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sion of groups he

### 15.4.5 Intram

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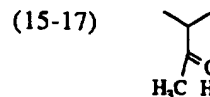
An example is  
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Another exam  
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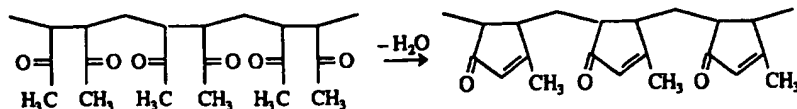
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at various keto gro  
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groups (Eq.(15-17)  
unreacted keto gro



The situation is  
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in intramolecular  
polymer with 5-me



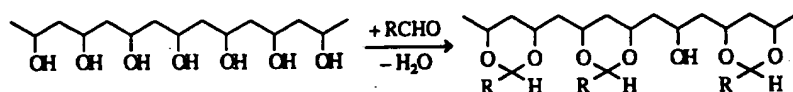
(15-18)



Similar statistical restrictions apply to *irreversible intermolecular* reactions of side groups of polymer molecules with bifunctional low molecular weight compounds. If all groups are exclusively in a 1,3-position (head-to-tail), a fraction of  $1/e^2 = 0.135$  cannot react according to statistical calculations (Appendix A-15; Table 15-2). In *equilibrium reactions*, however, the maximum conversion may reach almost 100 %.

An example is the acetalization of poly(vinyl alcohol) by aldehydes  $RCHO$  (Eq.(15-19)). For irreversible reactions of head-to-tail polymers, theory predicts a maximum group conversion of  $1 - (1/e^2) = 1 - (1/2.718^2) = 1 - 0.135 \rightarrow 86.5$  %. Experimental values were 85.8 % for chloroacetaldehyde, 85.0 % for palmitic aldehyde, and 83 % for benzaldehyde. The maximum conversion was considerably lower for aldehydes with ionizable groups, for example, 44 % for *o*-benzaldehyde sulfonic acid and 26 % for benzaldehyde disulfonic acid. Additional intermolecular reactions boost the conversion to more than  $1/e^2$ , leading to branched and crosslinked polymers.

(15-19)



Similar effects were also observed for the ketalization of poly(vinyl alcohol) by ketones. After 100 hours in dimethylsulfoxide at 25°C, maximum degrees of ketalization were 84.2 % for butanone, 80 % for cyclohexanone, 70.8 % for acetone, 59.5 % for dibutylketone, and only 34.7 % for di-*t*-butylketone.

Only a few cyclization reactions are used industrially. Poly(vinyl butyral) with a content of 80 % butyral groups, 18% hydroxy groups, and 2 % acetate groups is plasticized with 30 % dibutyl sebacate and used as an interlayer film for safety glass and as a primer for lacquer and varnishes. Cellulose acetate-*co*-butyrate contains 17-48 % butyral groups and 6-29 % acetyl groups. It serves for corrosion resistant packaging materials.

At elevated temperatures, natural rubber cyclizes by cationic polymerization of the double bonds; it simultaneously degrades. The resulting mono, di, and tricyclic structures are separated from each other by methylene groups of non-cyclic isoprene units. The resulting cyclorubber serves as a binder for printing inks, lacquers, and adhesives.

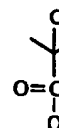
Table 15-2 Maximum theoretical fractions  $f$  of unreacted groups from the irreversible bifunctional reaction of substituents  $R$  with a probability  $p$  of constitutional diads of reactive groups.  $0 \leq p \leq 1$  for azeotropic copolymers but  $p = 1$  for homopolymers. H = head, T = tail.

Arrangement of monomeric units	Groups per mer	$0 \leq p \leq 1$	Fraction $f$ of unreacted groups if	
			$p = 0$	$p = 1$
H-T	1	$\exp(-2p)$	1	$\exp(-2) = 1/e^2 = 0.135$
H-T	2	$1 - p + (2/9)p^3 - \dots$	1	$1/(2e) = 0.184$
H-T, H-H, and T-T at random	2	$1 - (3/4)p + (5/72)p^3 - \dots$	1	0.312
H-H and T-T alternating	2	$1 - (1/2)p$	1	0.500

15 Reactions of  $M_1$ 

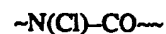
On heating will form methacrylim

(15-20)



## 15.4.6 Polymer

Polymer reagent are ion exchange proteins and peptides agents also includes. Examples of



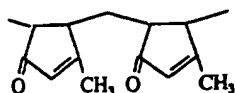
Most polymer groups. They can be used in the function of the functional polymerization to a sample of a crosslinking styrene and divinyl groups that are suitable, according to

The use of crosslinking products. The large capability to apply a sufficient polymer reaction sorbent for the product

Neighbor group those of low-molecular weight sample is the reaction log. The former can lead to an addition

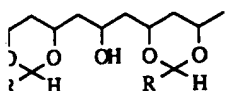
(15-21)





Similar reactions of side  
light compounds. If all  
of  $1/e^2 = 0.135$  cannot  
(15-2). In equilibrium  
1 %.

Aldehydes RCHO (Eq.(15-  
predicts a maximum  
6.5 %. Experimental  
dehyde, and 83 % for  
r for aldehydes with  
c acid and 26 % for  
boost the conversion



(vinyl alcohol) by ke-  
degrees of ketalization  
ketone, 59.5 % for di-

(1-butyl) with a con-  
e groups is plasticized  
glass and as a primer  
ins 17-48 % butyl  
packaging materials.

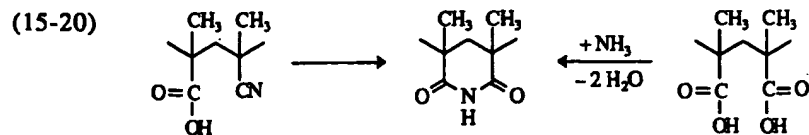
polymerization of the  
li, and tricyclic struc-  
cyclic isoprene units.  
ers, and adhesives.

reversible bifunctional re-  
active groups.  $0 \leq p \leq 1$  for

ected groups if  
 $p = 1$

$$\begin{aligned} \exp(-2) &= 1/e^2 = 0.135 \\ 1/(2e) &= 0.184 \\ &0.312 \\ &0.500 \end{aligned}$$

On heating with ammonia, copolymers of methacrylic acid and methacrylonitrile form methacrylimide units. The evaporating water expands the polymer to a hard foam:



### 15.4.6 Polymer Reagents

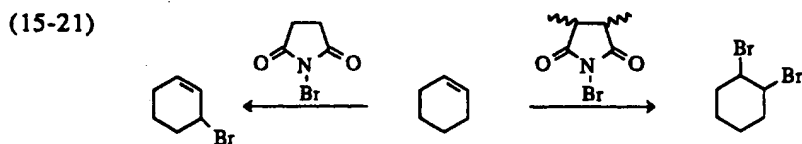
Polymer reagents are reagents composed of soluble or insoluble polymers. Examples are ion exchange resins (Section 15.4.3) and the resins for the Merrifield syntheses of proteins and peptides (Section 14.3.12) and nucleic acids (Section 14.2.7). Polymer reagents also include redox polymers (reduction-oxidation polymers) for electron transfers. Examples of polymer reagents and their reactions are

$\sim(p\text{-C}_6\text{H}_4)\text{-ICl}_2$	cis-chlorination of olefins;
$\sim(p\text{-C}_6\text{H}_4\text{N})\text{-BH}_3$	hydrogenation and reduction of aldehydes and ketones;
$\sim(p\text{-C}_6\text{H}_4)\text{-P=CRR'}$	Wittig reaction of aldehydes;
$\sim(p\text{-C}_6\text{H}_4)\text{-I(OOCCH}_3)_2$	oxidation of aniline to azobenzene;
$\sim\text{N(Cl)-CO}\sim$	oxidation of alcohols.

Most polymer reagents are crosslinked polymers that carry the desired functional groups. They can be synthesized by various strategies: direct crosslinking polymerization of the functional group-carrying monomer or, much more commonly, crosslinking polymerization to a "neutral" polymer with subsequent functionalization. A common example of a crosslinking polymerization is the free-radical suspension polymerization of styrene and divinylbenzenes (Volume II). An example of functionalization is the reaction of the resulting polymer beads with chlorodimethylether which delivers  $\sim\text{CH}_2\text{Cl}$  groups that are subsequently reacted further to the desired functional group, for example, according to  $\sim\text{CH}_2\text{Cl} + \text{LiP(C}_6\text{H}_5)_2 \rightarrow \sim\text{CH}_2\text{P(C}_6\text{H}_5)_2 + \text{LiCl}$ .

The use of crosslinked polymer reagents offers an easy separability of products and educts. The large concentration gradients in columns of such polymer reagents and the ability to apply a large excess of the educt increases the yield of the desired product. Efficient polymer reagents are easy to regenerate, stable against degradation, and non-adsorbent for the product. The latter can be achieved by using macroreticular networks.

Neighbor group effects do not always let reactions at polymer reagents proceed like those of low-molecular weight reagents. General rules obviously do not exist. An example is the reaction of cyclohexene with *N*-bromosuccinimide and its polymeric analog. The former causes a substitution reaction to bromocyclohexene whereas the latter leads to an addition of bromine to 1,2-dibromocyclohexane:



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